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Experimental investigation on the effect of O_2 and CO_2 on burning rates during oxyfuel combustion of methane

P. Heil, D. Toporov, M. Förster, R. Kneer *

Institute of Heat and Mass Transfer, RWTH Aachen University, Eilfschornsteinstraße 18, D-52062 Aachen, Germany

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Abstract

For combustion in an CO_2/O_2 atmosphere, known as oxy-combustion, altered combustion rates have to be expected. Previous investigations reported that this can be explained not only with the different thermo-physical and radiative properties, but also by the fact that CO_2 participates directly in the chemical reactions. This paper presents an experimental study on oxyfuel methane combustion with the aim to investigate the importance of the chemical effects of high CO_2 concentrations. Experiments have been carried out in a 25 kW furnace for flameless combustion which provides the possibilities to achieve stable combustion of methane within a wide range of oxygen concentrations in the CO_2/O_2 mixture at constant reactor temperature. This allows to focus on the chemical effects of CO_2 by keeping the remaining factors affecting the combustion rate constant. Four different oxidizer mixtures (CO_2/O_2 and N_2/O_2 both with 21 vol% and 18 vol% O_2) have been studied by detailed in-furnace measurements for flue gas compositions and temperature. In case of combustion in N_2/O_2 atmosphere, the CO profiles obtained for different O_2 concentrations overlap thus demonstrating that changing the O_2 concentration did not affect combustion rates, with keeping the temperature constant. In case of combustion in CO_2/O_2 atmosphere, the CO concentrations obtained were much higher than those in N_2/O_2 atmosphere. In contrast to N_2/O_2, the O_2 concentrations had a significant impact on the production and consumption rates of CO in oxyfuel combustion. The results obtained in this work demonstrated that by elimination of the influence of: molar heat capacity, CO_2 dissociation, and thermal radiation, it can be estimated that the observed effects of high CO_2 concentrations on combustion rates can be attributed to its participation in the chemical reactions. An increase of O_2 in oxyfuel led to a reduction of this impact, however, further investigations on the exact mechanism are necessary.

Keywords: Oxyfuel; Flameless combustion; CO_2; Reaction rates

1. Introduction

A number of options exist to reduce CO_2 emissions generated during the combustion of carbonaceous fuels. Combustion using oxygen instead of air as the oxidizer is considered as a valuable technology for low-cost CO_2 separation combined with reduction of conventional

* Corresponding author.
E-mail address: kneer@wsa.rwth-aachen.de (R. Kneer).

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pollutant emissions. Although it is theoretically possible to burn fuel (coal, petrol or gas) in pure oxygen, some degree of flue gas recycling is generally necessary for temperature control and material safety issues.

The combustion of fuel in a mixture of recirculated flue gas (RFG) and oxygen, however, presents new challenges to combustion specialists. Several experimental investigations with oxy-firing pulverized coal burners report that flame temperature and stability are strongly affected [1–3]. CO_2 features pronounced differences in thermodynamic and optical properties compared to air; it is therefore of vital importance for the efficient management of combustion processes to know the effect of the particular properties of CO_2 on the chemical reactions and the heat transfer that take place during oxy-combustion.

This paper focuses on the investigation of the oxy-combustion of methane. The substitution of N_2 with CO_2 in the oxidizer will lead to a reduction of the flame speed as reported by Zhu et al. [4]. This causes poor combustion performance and a modified distribution of temperature and species in the combustion chamber. The lower burning velocity for oxy-combustion of gaseous fuel theoretically can be affected by the following features: (1) lower thermal diffusivity of CO_2, (2) higher molar heat capacity of CO_2, (3) chemical effects of CO_2, and (4) modified radiative heat transfer.

Since the molar heat capacity affects the flame temperature, its effect generally dominates. The lower adiabatic flame temperature in oxy-combustion can be increased by increasing the oxygen concentration in the CO_2/O_2 gas mixture, thus reaching similar flame temperature levels as in air combustion [5,6].

Liu et al. [7] have performed numerical investigations on the chemical effects of CO_2. A comparison between numerical and experimental data showed, that the decrease in burning velocity for the oxyfuel combustion can not entirely be described by only considering the material properties of CO_2. CO_2 affects the combustion reactions especially by the reaction

$$CO + OH \leftrightarrow CO_2 + H \tag{1}$$

which reduces the concentration of important radicals as, e.g., H, O, OH in the combustion chamber and thus decreases the burning velocity. This hypothesis is supported by a comparison of the burning velocity of methane flames and hydrogen flames in a CO_2/O_2 gas mixture. The influence of CO_2 on the burning velocity of hydrogen flames is less significant because the concentration of hydrogen radicals is much higher. Finally, it was summarized, that the chemical effect of CO_2 significantly reduces the burning velocity of methane, where by the relative importance of this chemical effect increases with increasing CO_2 concentration in the oxidizing mixture.

Glarborg and Bentzen [8] did an experimental and theoretical analysis on the formation of CO in oxy-combustion of methane and found a strong increase of CO concentrations in the near burner region. CO_2 competes with O_2 for atomic hydrogen and leads to formation of CO through the reverse reaction of reaction (1).

Shaddix and Molina [9] have performed experiments on coal particle ignition. Equilibrium calculations showed that at the temperature of the experiments (1700 K) dissociation of CO_2 is very minor and therefore is unlikely to influence the volatiles ignition delay observed in CO_2 diluent. They also reported that a potential influence of CO_2 on ignition chemistry may stem from reduction of the primary CO oxidation rate in reaction (1), and enhancement of key recombination reactions such as $H + O_2 + M = HO_2 + M$. The chaperon efficiency of CO_2 in these recombination reactions is somewhere between two and three times that of N_2. These chemical kinetic effects are consistent with the observed increase in ignition delay in the CO_2 environments. Therefore it was unclear whether the primary effect of CO_2 on coal particle ignition results from its high specific heat, its tendency to suppress radical formation, or a combination of both.

The objective of present study is to assess the importance of the chemical effects of the high CO_2 concentration in oxyfuel combustion of CH_4 and to provide detailed experimental data obtained under well-defined reaction conditions such as in a reactor for flameless combustion. Using a flameless combustor provides the possibility to reduce the effects of molar heat capacity, CO_2 dissociation or thermal radiation on the combustion rate by keeping the reactor temperature constant for all the experiments performed through control of cooling system. Furthermore, due to its specifics, this combustion can achieve stable combustion of methane with less than 21 vol% oxygen in the CO_2/O_2 mixture as reported in [10] thus broadening the operation regime for stable combustion.

2. Experimental setup

Flameless combustion burners are well known in industrial high temperature combustion applications [11–13]. Due to the high momentum of the air inflow, intense mixing of fuel, oxidizer and hot flue gas occurs inside the combustion chamber. As a result, there is no flame attached to the burner. Instead, a large reaction zone with low oxygen content is generated thus promoting “distributed” reactions in the combustion chamber. The temperature and species distribution in the combustion chamber are uniform so that this combustion mode is considered to behave similarly as a perfectly stirred reactor [14,15].

Figure 1 shows a sketch of the test facility at RWTH Aachen University used for flameless gas combustion experiments. The furnace has a vertical, cylindrical geometry with a height of 1 m and an inner diameter of 0.55 m. The combustion chamber is air cooled to obtain a constant inner temperature without reducing the thermal load. This is achieved by cooling pipes which are mounted close to the wall.

The burner used is a commercial recuperative burner designed for flameless operation at a thermal load of 25 kW. It is installed at the bottom of the combustion chamber facing upward to minimize the influence of gravity on the flow. The hot flue gas leaves the combustion chamber through the recuperator of the burner thus heating up the incoming fresh gas mixture. Methane enters the furnace through a central opening in the front plate of the burner. This central opening is surrounded by six openings which supply the preheated oxidizer gas mixture, see Fig. 2. The burner and the experimental burning chamber were designed by WS Wärmeprozesstechnik GmbH.

A series of tests with different oxidizer mixtures have been carried out at a constant furnace wall temperature of 900 °C. Four different gas mixtures consisting of N_2/O_2 and CO_2/O_2 each with 21 vol% O_2 and 18 vol% O_2 (Air-21, Air-18, Oxyf-21, Oxyf-18) were used as oxidizer stream as shown in Table 1. All experiments were conducted at an oxygen/fuel ratio of 1.15, resulting in a constant volume flow of oxygen (5.78 m_N^3/h) for all tests.

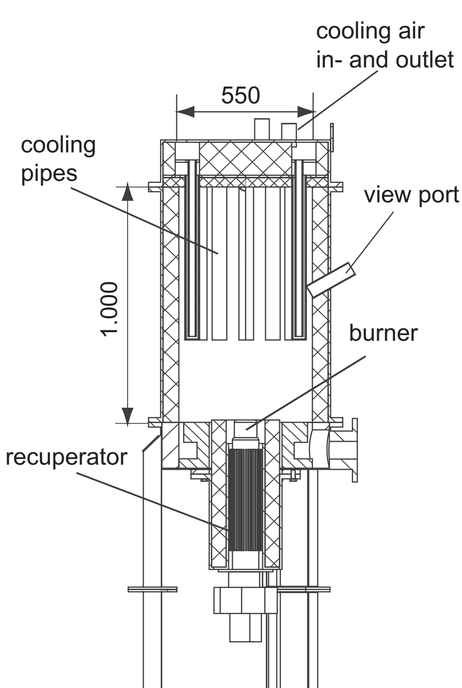

Fig. 1. Test facility.

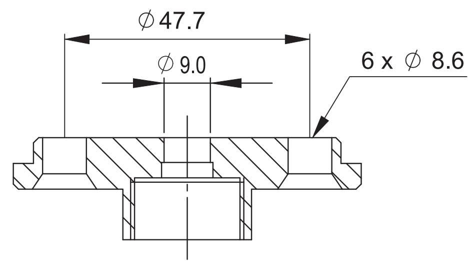

Fig. 2. Sectional drawing of the front plate.

Table 1
Oxidizer composition (O_2 volume flow was 5.78 m_N^3/h for all cases).

	N_2 volume flow (m_N^3/h)	CO_2 volume flow (m_N^3/h)
Air-18	26.35	0
Air-21	21.76	0
Oxyf-18	0	26.35
Oxyf-21	0	21.76

To investigate the influence of the different gas mixtures on the species and temperature distribution in the combustion chamber detailed in-flame measurements were made through an opening in the top of the combustion chamber. With a traverse system a probe was moved in an axial range of 0.05–0.95 m from the burner outlets and a radial range from 0 to 0.15 m from the middle of the furnace. In order to determine the influence of the composition of the oxidizer on the species distribution in the combustion camber an air cooled probe was used to take gas samples at different positions in the combustion chamber. The concentrations of O_2, CO_2 and CO in 10 radial and four axial positions (a total of 40 points) were measured. Additionally, a traversable probe with a thermocouple was used to measure the gas temperature at the same positions. CO and CO_2 were measured with non-dispersive ultraviolet absorption, the measurement principle of the O_2 analyser is of paramagnetic type. For the detailed temperature measurements a PtRh/Pt thermocouple type S was used. More details about the measurement equipment and the data evaluation are given by Heil [10].

In order to minimize the influence of the measurement's sequence, the order of the measurement position was selected randomly. The radial profiles presented were obtained during two measurements performed at two different days using two different sequences of measurement positions. For each position the measurement time selected was 2 min. The measured data are evaluated by

variance analysis. To assure clarity the confidence intervals are not shown in the graphs. They will be presented in Section 3.

3. Results and discussion

All the experiments were performed in flameless oxidation mode which was confirmed by optical observation. The experimental results obtained show stable combustion and a pronounced external recirculation zone thus corresponding to the definition of flameless oxidation given by Wünning [17].

The global mean values of oxygen concentrations measured at the combustion chamber exit are 2.7 vol% O_2 for Air-18 and Oxyf-18 and 3.0 vol% O_2 for Air-21 and Oxyf-21. The measured global CO levels were below the detection limit for all the cases, showing full burnout.

The measured values of flue gas temperature and gas concentrations averaged over 40 measurement point inside the combustion chamber are given in Table 2. The corresponding standard errors were ±5.6 °C, ±0.08 vol% and ±31 ppm for temperature, O_2 and CO concentrations, respectively.

The relatively small differences between the averaged temperature levels show constant temperature conditions during all experiments. The differences in the temperature levels between N_2/O_2 and CO_2/O_2 cases can be attributed to (i) precision of the experiment and of the measurement device, and (ii) the higher emissivity/absorptivity of CO_2 compared to N_2. However, the short path lengths of the furnace should minimize the effect of changed gas emissivity [16].

The difference in the O_2 concentrations in the oxidizer predetermines the different average O_2 levels obtained inside the combustion chamber. However, the difference of 3 vol% O_2 in the oxidizer causes a difference of about 1.2 vol% for air combustion and only about 0.4 vol% for oxyfuel combustion. Concerning the CO levels, it can be seen that for air combustion there is only a small difference between the cases Air-21 and Air-18. In oxyfuel combustion, however, the CO concentration is about twice as much for Oxyf-21 and about six times higher for Oxyf-18 as those obtained for air combustion. The interpretation of these results requires a more detailed look at the measured data.

The measured radial temperature profiles are plotted in Fig. 3. The 95% confidence interval for all measurement points is ±20 °C. The radial profiles of the temperature measured for all cases are very similar thus showing similar heat release due to combustion. Close to the burner, at an axial distance of 0.2 m, the temperature difference between the radial positions 0 and 0.15 m is about 200 °C reflecting the initial heating of the incoming fuel–oxidizer mixture. This difference decreases with increased distance from the burner approaching 50 °C at 0.8 m axial distance. The slow rise of gas temperature and the small temperature gradients suggest a continuous reaction which is typical for flameless combustion. Between a radial position

Table 2
Measured values of flue gas temperature and gas concentrations averaged over 40 measurement points inside the combustion chamber.

	Temperature (°C)	O_2 (vol%), dry	CO (ppm), dry
Air-18	903	4.2	196
Air-21	877	5.4	206
Oxyf-18	926	4.4	1359
Oxyf-21	904	4.8	591

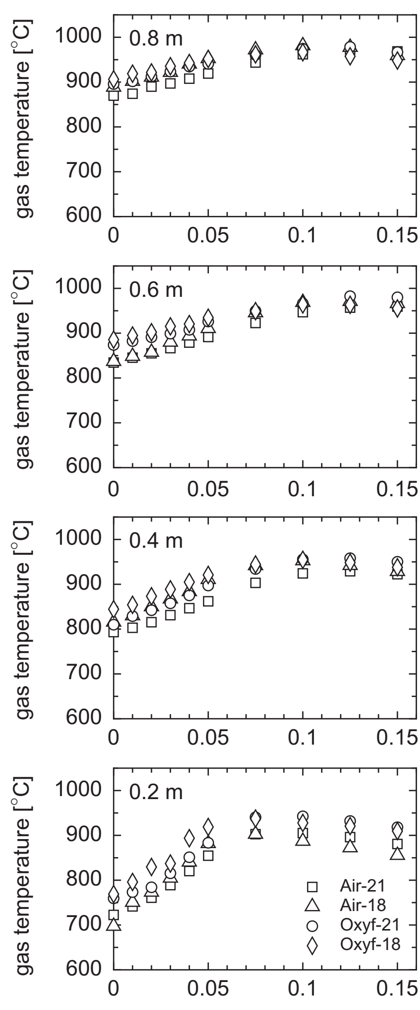

Fig. 3. Detailed temperature measurements at different burner distances.

of 0.1 m and the edge of the combustion chamber the flue gas is recirculated back to the burner. This can be seen also from the O_2 profiles shown in Fig. 4 (95% confidence interval ±0.05 vol%).

For all settings and axial positions the maximum of the O_2 concentration is located in the middle of the combustion chamber showing the main fuel/oxidizer jet. Close to the burner, at an axial distance of 0.2 m, the measurements show a decrease of O_2 concentrations in the region between the centerline and 0.1 m radial distance. In the outer region, between 0.1 and 0.15 m, the O_2 profile becomes uniform thus showing the recirculation zone. With increased distance from the burner the O_2 profiles flatten.

The measurements of gas temperature and O_2 concentrations show a reaction zone in the middle of the combustion chamber between radial positions of 0 and 0.1 m. In this area the gas temperature increases and the O_2 concentration decreases with increasing burner distance. The flue gas is recirculated back to the burner in the recirculation zone formed at radial positions lager than 0.1 m. In this area the O_2 concentration is more uniform indicating much slower reaction rates.

The CO concentrations measured for air and oxy-combustion are given in Figs. 5 and 6 for air and oxyfuel, respectively. The 95% confidence interval for all measurement points is ±394 ppm. Higher CO concentrations are measured in the recirculation zone where the CO oxidation actually takes place, for both types of combustion (air and oxyfuel). However, the levels obtained for air and oxyfuel cases are quite different.

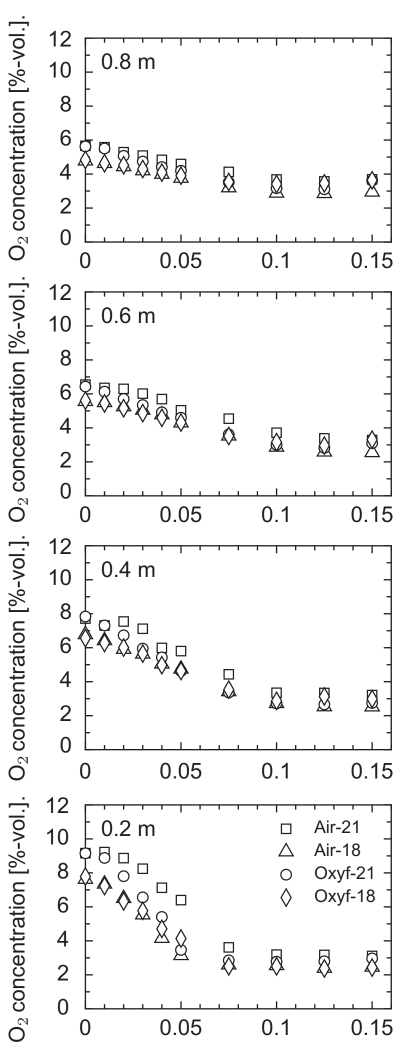

Fig. 4. Detailed O_2 measurements at different burner distances.

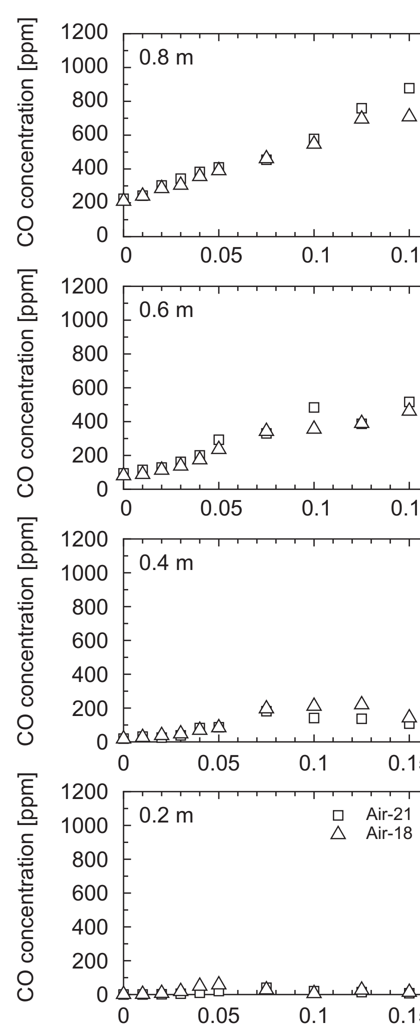

Fig. 5. Detailed CO measurements at different burner distances for air combustion.

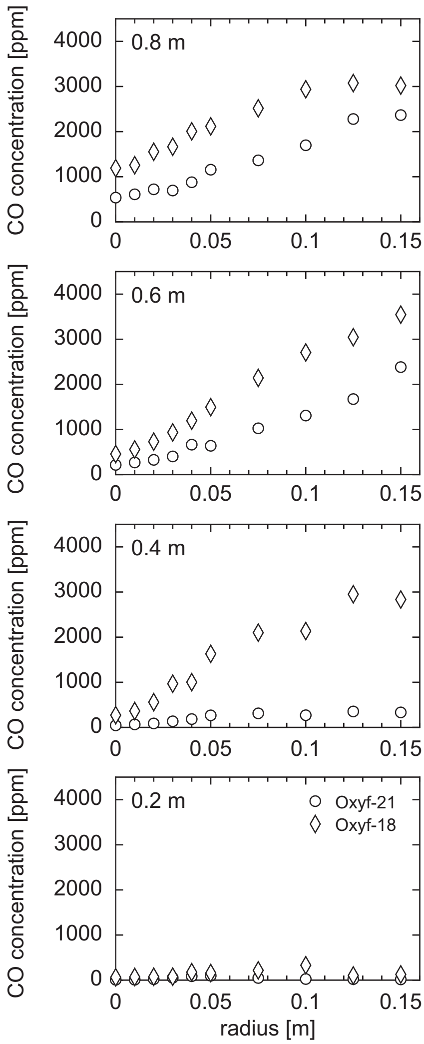

Fig. 6. Detailed CO measurements at different burner distances for oxyfuel combustion.

In case of air combustion the measured CO profiles overlap, thus demonstrating no influence of O_2 concentration on the CO production and oxidation rates when the temperature is constant. At a burner distance of 0.2 m the CO concentrations are negligibly low. This means that the production of CO in the main jet stream did not start yet and the oxidation of the already produced CO is completed in the recirculation zone. With increasing burner distance the CO concentration increases, with the highest level of 800 ppm measured at an axial distance of 0.8 m and a radial position of 0.15 m.

In case of oxyfuel combustion, however, the measured CO profiles differ for the two investigated cases. Similar to air combustion, the measured CO levels for both settings at the axial position 0.2 m are low. At a burner distance of 0.4 m there is already a significant increase in CO levels for the Oxyf-18 case. The minimum values measured at this axial distance (about 200 ppm) are obtained in the center of the combustion chamber whereas the maximum (about 3000 ppm) are obtained at a radial position of 0.15 m. In comparison, the CO concentrations measured at this axial position for the Oxyf-21 case stay below 300 ppm. With increased burner distance the level of CO increases for both settings with CO levels for Oxyf-21 being about two times lower than those obtained for Oxyf-18 case. The higher CO levels obtained for Oxyf-18 in the reaction zone in the middle of the combustion chamber shows higher CO production rates than in Oxyf-21. Furthermore, the CO profiles for the settings of Oxyf-18 measured in the recirculation zone between the burner distances 0.4 and 0.6 m show almost identical values, whereas in case of Oxyf-21 the CO levels drop rapidly. This shows a significant effect of the O_2 concentration on the oxidation rates of CO in oxyfuel combustion.

4. Conclusion

An experimental investigation of flameless methane combustion in different atmospheres (N_2/O_2 and CO_2/O_2) and O_2 concentrations (21 vol% and 18 vol%) involving detailed in-flame measurements was carried out.

The measurements of gas temperature obtained for all settings show uniform temperature distribution and negligible differences between the cases. The measured O_2 concentrations show a similar trend in the radial profiles for all cases. The levels of the O_2 profiles differ depending on the O_2 concentration of the oxidizer.

The CO levels measured for N_2/O_2 atmosphere are identical, thus showing that there is no influence of O_2 concentration on the CO production and oxidation rates when the temperature is constant. In CO_2/O_2 atmosphere, however, an increase of O_2 concentrations from 18 vol% to 21 vol% leads to a reduction of almost two times of the measured CO levels in the reaction zone, thus showing lower CO production rates than in Oxyf-18. Furthermore, the development of the CO levels in the recirculation zone shows a significant effect of the O_2 concentration on the oxidation rates of CO in oxyfuel combustion.

Summarizing, the results obtained in this work demonstrated the following: by elimination of the influence of: (1) molar heat capacity (by keeping furnace temperature constant for all cases), (2) CO_2 dissociation (by keeping furnace temperature at max 900 °C), (3) thermal radiation (by performing experiments in a small scale furnace at constant and low temperature), it can be estimated that the chemical effects of CO_2 presence have a

significant impact on the production and consumption rates of carbon monoxide in oxyfuel combustion. An increase of O_2 in oxyfuel can reduce this impact, however, further investigations including mathematical description are needed to clarify and assess this effect.

The results of this work can be used for verification of gas-phase combustion schemes when modeling combustion in an oxyfuel environment.

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